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Division of Synthetic Chemistry – Organoelement Chemistry –

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Scope of Research

Organic chemistry has mainly developed with the use of second-row elements such as carbon, oxygen, and nitrogen, while the synthesis and isolation of the heavier congeners of typical organic molecules as stable compounds has been a dream for organic chemists. Our main research interest is the elucidation of the similarities and differences in structures and reactivities between organic compounds and the corresponding heavier congeners. These studies are interesting and important from the standpoints of fundamental chemistry, and open the way to more extensive application of main group chemistry.

KEYWORDS

Steric Protection Kinetic Stabilization Low-coordinated Species
Heteroatom Transition Metal Complexes



Selected Publications

- Nagata, K.; Murosaki, T.; Agou, T.; Sasamori, T.; Matsuo, T.; Tokitoh, N., Activation of Dihydrogen by Masked Doubly Bonded Aluminum Species, *Angew. Chem. Int. Ed.*, **55**, 12877-12880 (2016).
- Suzuki, Y.; Sasamori, T.; Guo, J.-D.; Nagase, S.; Tokitoh, N., Isolation and Ambident Reactivity of a Chlorogermolenoid, *Chem. Eur. J.*, **22**, 13784-13788 (2016).
- Agou, T.; Ikeda, S.; Sasamori, T.; Tokitoh, N., Synthesis and Structure of Lewis-Base-Free Phosphinoaluminum Derivatives, *Eur. J. Inorg. Chem.*, **2016**, 623-627 (2016).
- Sasamori, T.; Villalba Franco, J. M.; Guo, J.-D.; Sugamata, K.; Nagase, S.; Streubel, R.; Tokitoh, N., Selenium-Substituted Phosphaalkenes Obtained through 1,2-Elimination of Chlorosilanes from Selenenylchlorophosphines, *Eur. J. Inorg. Chem.*, **2016**, 678-684 (2016).
- Sugahara, T.; Guo, J.-D.; Sasamori, T.; Karatsu, Y.; Furukawa, Y.; Ferao, A. E.; Nagase, S.; Tokitoh, N., Reaction of a Stable Digermene with Acetylenes: Synthesis of a 1,2-Digermabenzene and a 1,4-Digermabarrelene, *Bull. Chem. Soc. Jpn.*, **89**, 1375-1384 (2016).

Activation of Dihydrogen by Masked Doubly Bonded Aluminum Species

Activation of dihydrogen (H_2) with transition-metal complexes is an important fundamental chemical transformation and has been extensively investigated for several decades. In contrast, main-group element compounds had been considered as ineffective for the splitting of H_2 for a long time, until the discoveries of the catalyst-free hydrogenation of heavier Group 14 triply bonded compounds, dimetallynes, and of the frustrated Lewis pair (FLP)-catalyzed hydrogenation. Thereafter, H_2 activation using multiply bonded and low-coordinate compounds of heavier main-group elements have been reported. Among various heavier main-group elements, aluminum is a promising candidate as the key component of the H_2 activation reagents, as shown by the recent reports on small-molecule activation with aluminum-based FLPs.

We have already reported the reactivity of barrelene-type dialumane **1** as the masked form of 1,2-diaryldialumene **2**. At ambient temperature, **1** most certainly undergoes retro [2+4] cycloaddition to generate **2**, which can be trapped by various trapping reagents. These findings are indicative of the possibility of H_2 activation by using **1** as the masked forms of the corresponding dialumenes **2**.

Reactions of **1** with H_2 afforded dihydroalumanes $ArAlH_2$ at room temperature (Ar: bulky aryl groups).

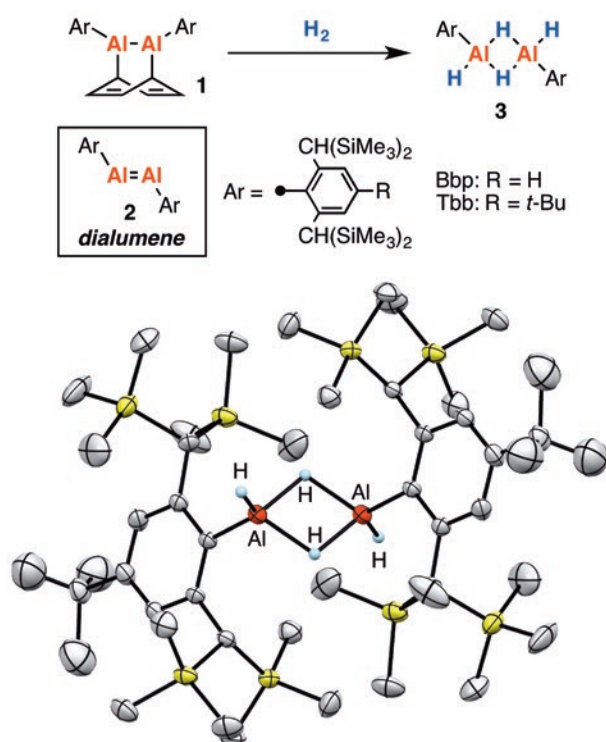


Figure 1. Reactions of barrelene-type dialumane **1** with dihydrogen and the Structure of **3** (Ar = Tbb).

These dihydroalumanes form hydrogen-bridged dimers $[ArHAL(\mu-H)]_2$ **3** in the crystalline state, while a monomer–dimer equilibrium was suggested in solution. Dialumenes **2** generated from **1** are the putative active species in the cleavage of H_2 .

Isolation and Reactivity of a Chlorogermyl-enoid

Metallylenoids of the general formula R_2EXM (E = group 14 element, X = anionic leaving group, M = metal) represent the silicon analogs of carbenoids (R_2CXM), which may exhibit both carbanion (R_2CX^-) and carbene ($R_2C:$) character. Silylenoids (R_2SiXM) as well as silylenes ($R_2Si:$) have been postulated as important intermediates in the reduction of dihalosilanes towards silylenes and/or oligo- and polysilanes. In contrast to the variety and rich chemistry of halosilylenoids, heavier halogermynenoid (R_2GeXM) analogs and their associated chemistry still remains scarce.

Treatment of 2,5-di(3,5-*tert*-butylphenyl)-1-lithioferrocene (Fc^*Li) with $GeCl_2 \cdot dioxane$ afforded the corresponding chlorogermynenoid that exhibited an ambident reactivity in different solvents; it displayed a behavior characteristic for a dichlorogermylene anion in THF, while it exhibited the typical reactivity of a chlorogermylene in toluene. X-Ray diffraction analysis of a single crystal of this chlorogermynenoid, obtained from recrystallization in THF, revealed a separated-ion-pair structure in the solid state.

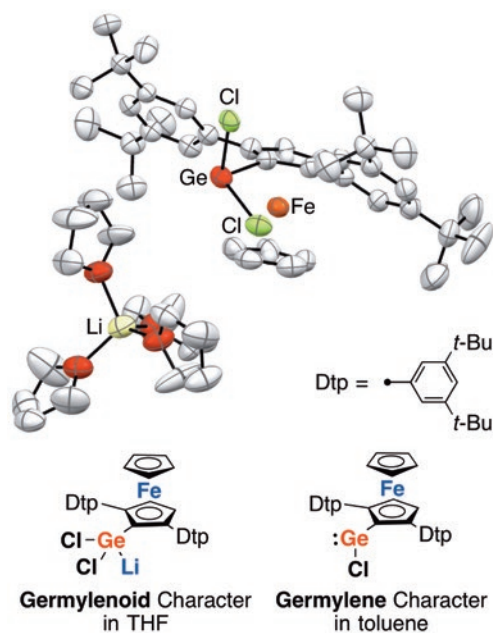


Figure 2. The structure of $[Li^+(thf)_4][Fc^*GeCl_2]^-$.